



Magnesium Repair by Cold Spray

by V. K. Champagne, P.F. Leyman, and D. J. Helfrich

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Weapons and Materials Research Directorate, ARL

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14. ABSTRACT <p>The U.S. Army has experienced significant corrosion problems with magnesium alloys that are used to fabricate aircraft components. The most severe of these are associated with large and expensive transmission and gearbox housings for rotorcraft, which have to be removed prematurely because of corrosion. Many of the parts cannot be reclaimed because there is not an existing technology that can restore them adequately for service. The U.S. Army Research Laboratory has developed a cold spray process to reclaim magnesium components that shows significant improvement over existing methods and is in the process of qualification for use on rotorcraft. The cold spray repair has been shown to have superior performance in the tests conducted to date, is inexpensive, can be incorporated into production, and has been modified for field repair, making it a feasible alternative over competing technologies. Cold spray trials were performed using aluminum powders at different deposition conditions with both helium and nitrogen carrier gas. Evaluations of the resultant cold spray aluminum coatings deposited on ZE-41A magnesium alloy substrates were conducted using microstructural analysis, hardness, bond strength, and corrosion testing.</p>				
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1. Objective

The development and qualification of the cold spray process to deposit commercially pure aluminum (CP-Al) was recommended by the U.S. Army Research Laboratory (ARL) Center for Cold Spray Technology (ARL-CCST) for providing dimensional restoration and protection to magnesium (Mg). The cold spray process was viewed as the best possible method for depositing aluminum (Al) coatings onto Mg and would be viewed as part of an overall strategy of replacement of the environmentally unacceptable chromate processes, such as Dow 17 and MIL-M-3171, currently in use today, eliminating environmental and worker safety issues, while significantly improving performance and reducing lifecycle costs.

2. Introduction

The widespread use of Mg in aircraft occurred during the Vietnam era to reduce weight and increase performance (1). Mg is approximately 35% lighter than Al and has exceptional stiffness and damping capacity (2). Therefore, Mg alloys, because of their high strength-to-weight characteristic, are used for the fabrication of many components on U.S. Department of Defense (DoD) aircraft, especially for complex components such as transmission and gearbox housings on helicopters and gearbox housings on fixed-wing aircrafts.

Mg is a very active metal electrochemically and is anodic to all other structural metals. Therefore, it must be protected against galvanic corrosion in mixed-metal systems because it will corrode preferentially when coupled with virtually any other metal in the presence of an electrolyte or corrosive medium (3). Many of the corrosion problems associated with Mg helicopter components occur at the contact points between ferrous metal inserts or mating parts, creating galvanic couples (4). Much of the corrosion occurs at attachment points where a dissimilar metal is in contact with the coated Mg component. This includes flanges, mounting pads, tie rods, lugs, and mounting bolts. Figure 1 is a schematic of the main transmission housing for the H-60 helicopter showing the areas most susceptible to corrosion. Figure 2 shows the extent of localized corrosion damage on one of the mounting pads after one overhaul cycle.

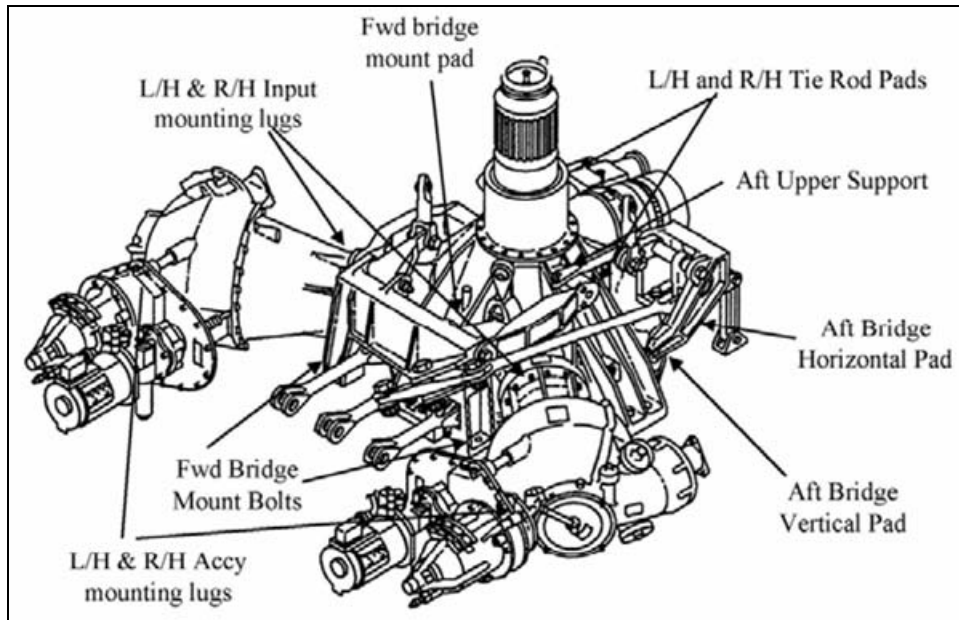


Figure 1. Schematic of H-60 main transmission housing.

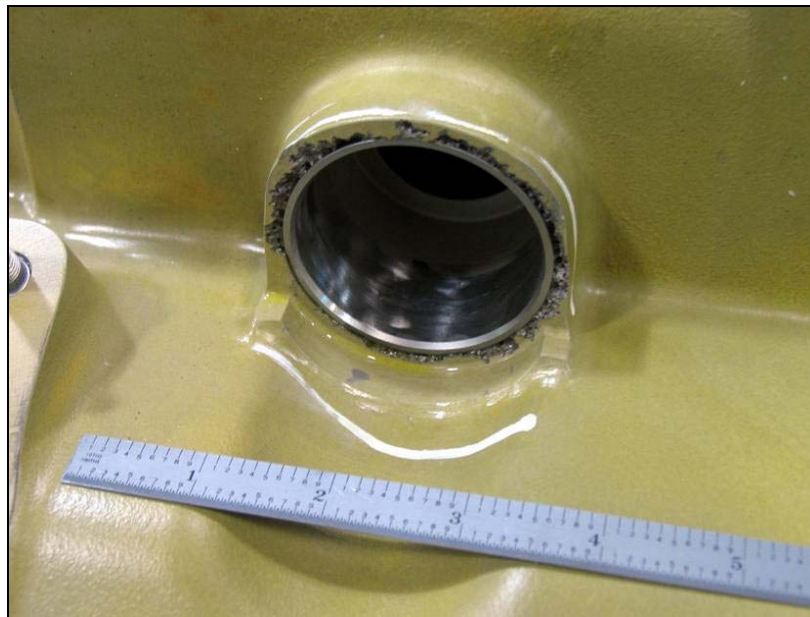


Figure 2. Corroded area on a Mg transmission housing.

Because of the localized nature of the corrosion, surface treatments intended to mitigate the problem would only have to be applied in these specific areas. In addition, Mg alloys are very susceptible to surface damage due to impact, which occurs frequently during manufacture and/or overhaul and repair. Scratches from improper handling or tool marks can result in preferential corrosion sites. The DoD and the aerospace industry have expended much effort over the last two decades to develop specific surface treatments to prevent corrosion, to increase surface hardness, and to combat impact damage for Mg alloys in order to prolong equipment service life (5);

however, the means to provide dimensional restoration to large areas on components where deep corrosion has occurred remains a challenge. The application of cold spray deposition for the repair of Mg corrosion and other damage is investigated in this effort.

3. Cold Spray Deposition System

The ARL-CCST currently maintains a high pressure stationary cold spray system manufactured by Ktech Corporation as well as four portable cold spray systems. Two of the portable cold spray systems were manufactured by Dymet, Inc., one by Centerline, and the remaining system was produced at ARL. All of the portable systems are considered low pressure with the exception of the ARL system, which can operate at low or high pressures. The work performed under this program was conducted with the Ktech System and the portable ARL system.

3.1 Cold Spray Nozzle Design

The conventional cold spray nozzle that is used with the Ktech System is normally fabricated from stainless steel or tungsten carbide (WC). Various nozzle configurations have been designed and tested at ARL and it is not the intent of this work to repeat the research of others but rather to relate those aspects of nozzle design specific to this application. The primary concern was clogging of the nozzle while spraying CP-Al. Clogging can occur in the throat of the DeLaval-type nozzle, where higher temperatures are employed. Al particles tend to stick to the sides of the steel nozzle interfering with proper gas flow, which adversely affects coating deposition. To mitigate clogging, a thermoplastic nozzle was used with success. ARL and others have conducted studies of various nozzle configurations and materials. Comparisons have been made of nozzles fabricated from ceramic, plastic, carbide, and other metallic materials. A nozzle fabricated from a high temperature-resistant thermoplastic was operated at 400 °C with satisfactory results without nozzle clogging. There are several thermoplastics on the commercial market that can be successfully machined and used as a nozzle material. Such thermoplastics can maintain their properties at high operating temperatures (400 °C) and are adequately wear resistant for use with CP-Al for extended periods of time. These plastics tend to be proprietary in nature but can be obtained from the cold spray equipment manufacturers.

3.2 Selection of Gases

The decision to use helium over nitrogen depends primarily on the benefits versus the added costs involved. However, from a technical standpoint the velocities that can be achieved by helium and the resultant improved density of the coatings may well be worth the extra cost, especially for components that are valued at \$400,000 each. During operation at ARL, the Ktech cold spray system uses 40 scfm of nitrogen at a cost of \$0.29/100 scf for a gas operating cost of \$0.116 per min. With helium, it uses 70 scfm at a cost of \$11.50/100 scf for a gas operating cost of \$8.05 per min. Therefore, the costs are substantially lower when using nitrogen. To put the gas

costs into perspective, the labor rate for operating a cold spray system is about \$1.00/min and the powder costs are about \$2.00/min. Helium recycling systems that have been designed and put into use are able to recover approximately 90% of the helium, thereby greatly lowering the operating cost (7). For a research and development (R&D) cold spray facility that operates intermittently, the cost of a recycling system cannot be justified. But for a production cold spray facility, the payback time on the cost of a recycling system would be fairly short for these expensive components. Nevertheless, the results of this work demonstrated that nitrogen can be used as a carrier gas to produce satisfactory cold spray coatings of CP-Al.

3.3 Powders

J. Vlcek et al. (8) has provided extensive information related to the physical processes that occur during the cold spray deposition of different materials and why some work better than others. Impact heating, equations of state during impact, dynamic yielding of the particles, and impact pressures were examined and it was concluded that the materials that are most amenable to cold spray are those with a face-centered cubic crystal structure, which includes Al.

The powders under consideration for the cold spray repair of Mg transmission housings are CP-Al, Al-12% silicon alloy (Al-12Si), and Al alloy 5056 (Al 5056). The requirements associated with this application are that galvanic corrosion and corrosion pitting are the primary causes for removing the components from service. In addition, any repair must be confined to nonstructural areas of the transmission and gearbox housings.

The Al 5056 (composition Al-5Mg-0.1manganese (Mn)-0.1chromium (Cr)) was considered because it is compatible with Mg and has better tensile, yield, elongation, and fatigue strength than any Mg alloy. The corrosion resistance of Al 5056 is also among the best of any Al alloy. The presence of the Mn is important, because it serves to tie up any residual iron contamination, which has been shown to degrade corrosion performance. Unfortunately, Al 5056 is an example of a powder that is not commercially available. The stock material used in the melt of the AL 5056 powder was also not available, forcing the powder manufacturer to purchase and subsequently mix the raw materials to produce the alloy prior to atomization. As a result, Al-12Si alloy was chosen as a candidate, based upon its excellent mechanical properties and resistance to wear and corrosion. These powders are commercially available and are used extensively with thermal spray.

Initially, concern was expressed over CP-Al as the material of choice for the cold spray repair of Mg ZE-41A because it was lower in hardness and strength than other Al alloys that were also being considered for this application. It was later selected since the primary reason that the Mg components were removed from service was due to corrosion and not wear, and the cold spray repair was to be performed on nonstructural areas of the component, making the strength requirement less of an issue. Additionally, the CP-Al powder could be doped with a certain

percentage of hardened particles to impart wear resistance if required. The cost of CP-Al is attractive at approximately \$11.00/lb and is commercially available, while many other alternative alloys originally considered were much more expensive and/or had to be produced as a specialty item.

Finally, the spherical particle shape of the CP-Al powder was preferred over that of the Al 5056 flake. Spherical particles form a more densely packed structure when deposited by the cold spray process resulting in better protection for the Mg substrate. Figure 3 shows micrographs of the two powder types.

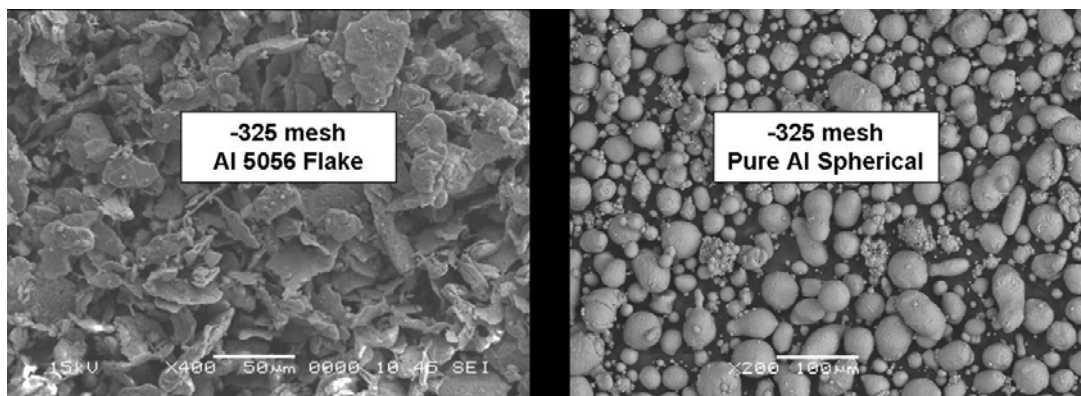


Figure 3. Particle shape effects on deposition.

3.4 Predictive Modeling for Process Optimization

The nature of the bond created during particle consolidation and the properties of the material produced by the cold spray process have been modeled at ARL. These predictive models are used to establish and optimize cold spray process parameters. Modeling efforts predict the amount of mixing at the interface between the particles and the substrate with concomitant high coating adhesion when the particle velocity exceeds a certain threshold value.

Compressible, isokinetic flow equations are used to model gas flow within the nozzle. Modified drag and heat transfer coefficients are then used to iteratively calculate the resulting particle velocities and temperatures. An example of this calculation for the Al/helium nozzle acceleration is shown in figure 4. The mean particle size for this calculation is 20 μm , and the initial gas pressure and temperature are 2.75 MPa and 20 $^{\circ}\text{C}$, respectively. Calculated particle velocities are verified experimentally by means of a dual-slit, laser velocimeter.

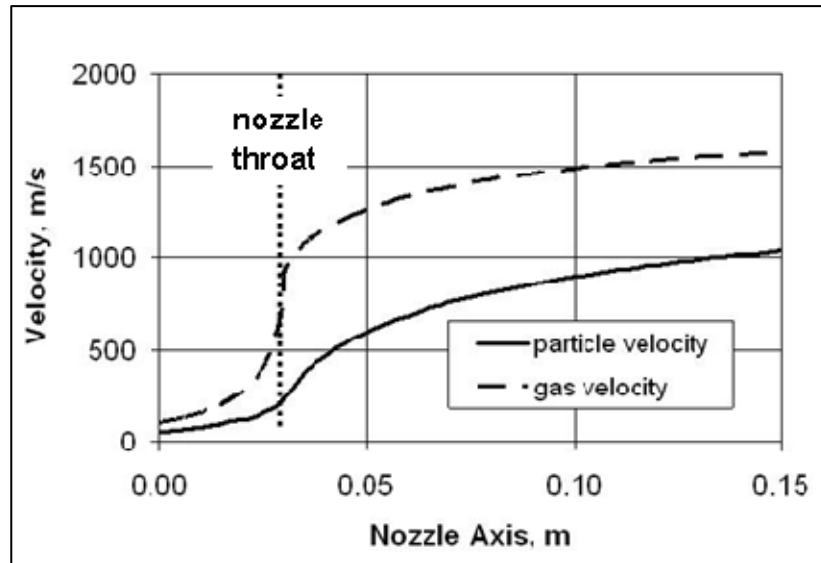


Figure 4. Example of 20 μm Al particles accelerated by helium.

An empirical relationship of the penetration of micrometeorites into spacecraft skin is used to model the interface between the deposit and the substrate, and an empirical relationship between particle characteristics and critical velocity is used to model deposition efficiency (9).

The demonstrated prediction accuracy of these calculations allows the ability to define operating parameter values and expected coating characteristics prior to cold spray operation. This prediction algorithm was subsequently used on multiple coating/substrate combinations with favorable results.

4. Parameter Selection

A series of cold spray trials were performed to optimize coverage, adhesion, and coating integrity. Each trial run required the specification of the powder, powder feed rate, gas, gas pressure, and gas temperature. Gas pressure and temperature were specified by model calculations to produce sufficient particle velocity for good deposition. Subsequent coating evaluation prescribed changes to the operating conditions if coating characteristics needed improvement.

A stationary and a portable cold spray system were used in these tests. A schematic of each system is shown in figure 5. The stationary system, supplied by Ktech, allows for the range of operation parameters given by table 1. Because the portable system does not have a gas heater, nitrogen gas cannot be used, as unheated nitrogen gas cannot achieve the required particle acceleration. The operating limits for the portable system are also given in table 1.

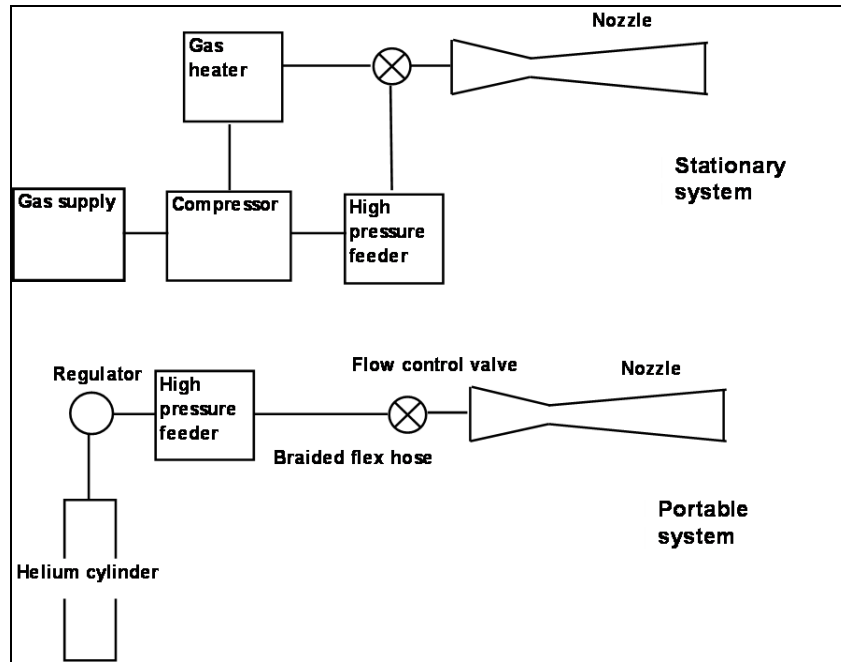


Figure 5. Stationary and portable cold spray system schematics.

Table 1. Cold spray operating parameters.

Parameter	Stationary System	Portable System
Gas	nitrogen, helium	helium
Gas pressure	1–2.74 MPa	1–2.74 MPa
Gas temperature	20–500 °C	20 °C
Powder feed rate	1–50 gm/min	1–5 gm/min

Besides the process limitations imposed by maximum allowable temperature and pressure, two operational restrictions narrowed the available parameter range—these were nozzle fouling and ambient temperature gas (for the portable unit). Low melting point powders can stick to nozzle walls, eventually plugging the nozzle. This is especially true for Al powders, but limiting gas heating to lower temperatures can prevent nozzle fouling.

Cold spray trials were carried out within the parameter limits listed in table 1, in order to determine optimum spray conditions for the two systems. As expected, higher gas pressures and temperatures produced the best coatings, where the coatings were evaluated by the methods described in section 5. In addition, it was found that helium gas produced superior coatings as compared to nitrogen when using a conventional nozzle fabricated from stainless steel or WC. However, fouling occurred whenever temperatures in excess of 250 °C were used with conventional nozzles. It was, therefore, necessary to conduct similar studies incorporating a

plastic nozzle. Higher gas temperatures could be attained without nozzle fouling through the use of plastic nozzles, and denser deposits with significantly increased bond strength were achieved. Optimum conditions determined by these tests are given in table 2.

Table 2. Optimum conditions.

Parameter	Stationary System (Standard Nozzle)	Portable System (Standard Nozzle)	Stationary System (Plastic Nozzle)
Gas	helium	helium	nitrogen
Gas pressure	2.74 MPa	2.74 MPa	2.74 MPa
Gas temperature	250 °C	20 °C	400 °C
Gas flow rate	122 m ³ /h	41 m ³ /h	39 m ³ /h
Powder feed rate	3 gm/min	1 gm/min	3 gm/min
Stand-off distance	25 mm	10 mm	25mm
Particle GMD	20 µm	20 µm	15 µm

Note: GMD = geometric mean diameter

5. Screening Tests

5.1 Coating Characterization

The mechanical properties, corrosion resistance, and microstructural features of the CP-Al cold spray coatings were analyzed. A discussion of the test methods employed and the results obtained are provided in this section. The use of special surface preparation techniques, test fixtures, specimen geometry, or other procedures that affect test results will provide valuable insight to those wishing to gain a better understanding of the evaluation of cold spray coatings. Bond strength and corrosion resistance were used as the primary screening tests to qualify the use of cold spray for this application.

5.2 Bond Strength

The adhesive strength (strength of the bond between the coating and the substrate) and cohesive strength (strength of the bond between particles) of the cold spray coatings were determined to be an important factors in the qualification of the cold spray process for use on Mg by the aerospace community. A major problem associated with the application of thermal spray coatings onto Mg is the formation of oxides on the surface of the substrate that adversely affects adhesion. Mg is a highly reactive material and is very susceptible to oxidation. Conventional thermal spray processes involve preheating the powders to a semi-molten state prior to being deposited onto the substrate. An advantage of the cold spray process for this application is that the powders are not heated sufficiently to cause the formation of a deleterious oxide layer.

Adhesion of the cold spray coatings was measured according to American Society for Testing and Materials (ASTM) Standard C 633-79. Since bond bars made of ZE41A Mg were not available, 2.5 cm diameter plugs cut out of 0.65 cm thick Al-coated ZE41A Mg coupons were bonded to the 2.5 cm diameter 6061-T6 Al bond bars. Each of the bond bars were threaded on one end so that they could be inserted into the test fixtures of a tensile test machine. The bond bar assembly is shown in figure 6. In the first step of this test, a cold spray coating was deposited onto the ZE41A Mg coupon that had been lightly abraded with 60 grit aluminum oxide (Al_2O_3). It is essential that virgin, uncontaminated grit be used, which is not contaminated with extraneous particulate matter, such as iron, that could become imbedded into the substrate and then affect adhesion or corrosion test results. The main purpose of the surface cleaning operation is to remove the magnesium oxide layer and expose fresh metal in order to facilitate the bonding mechanism. The cold spray coating was applied immediately afterward. Further process development negated the requirement of grit blasting but the fact remains that the surface of the substrate should be free from oxide and debris for optimal adhesion.



Figure 6. Bond bar adhesion test configuration.

The front and back surface of the cold spray coated plug was grit blasted in addition to both surfaces of the Al bond bars. A 2.5 cm diameter disk of FM-1000 adhesive is placed between both bond bar/plug contact areas and subsequently placed in a fixture to hold them together while the adhesive cures for 3 h at 150 °C. The adhesively bonded bars are then threaded into the cross-heads of a tensile test machine and pulled apart. The failure loads are measured and converted to tensile strength. This test is preferred over the conventional “dolly” or the “Patti”

test where 2.5 cm diameter plugs are bonded to a coated test panel because the bond bar test conducted with the use of a tensile test machine best insures that uniaxial tensile force is maintained throughout the duration of the test. The method also eliminates the risk of excess adhesive seeping out from around the edges of the plugs that, in turn, can bias the test results by increasing the effective cross-sectional area being tested, thus yielding erroneously higher adhesion values. The FM-1000 adhesive is also recommended because it does not easily migrate through open porosity down to the substrate, which can also result in invalid adhesion values.

The averaged test results shown in table 3 revealed that in all instances where helium was used as the accelerating gas the glue failed before the coating. Therefore, the reported adhesive strengths represent that of the glue and those of the coating are higher. In the test trial where nitrogen was used with a WC nozzle inlet section the values were significantly lower as a result of the lower particle velocities achieved since 300 °C gas temperatures were used to prevent nozzle clogging. In order to achieve higher gas temperatures (400 °C) without clogging of the nozzle a plastic nozzle was incorporated with satisfactory results as table 3 indicates. The results show that increased adhesion values were achieved with nitrogen at 400 °C and by means of applying a thinner coating per pass.

Table 3. Adhesion values of CP-Al deposited by the cold spray process.

Program	Conditions	Adhesion (MPa)	Failure Mode	Microns/Pass
ARL-DSTO	N ₂ , 2.74 MPa, 300 °C	19.1	Adhesive	508
ARL-DSTO	He, 2.74 MPa, 20 °C	>45.0	Glue failure	64
ARL-NCMS	He, 2.74 MPa, 20 °C	>58.6	Glue failure	177
ARL	N ₂ , 2.74 MPa, 400 °C	>59.8	Glue failure	64

Note: DSTO = Defense Systems and Technology Operation and NCMS = National Center for Manufacturing Sciences.

5.3 Hardness

The hardness of the cold spray coatings of CP-Al were measured from metallographic cross-sections with a Wilson Tukon Micro-Hardness Tester utilizing a load of 500 g and a diamond indenter. The values obtained were converted to Brinell for comparative purposes. Figure 7 shows a comparison between annealed and fully worked wrought Al to that of a CP-Al cold spray coating (10). It is important to note that the values of the cold spray coating were significantly higher than what were achieved by conventional materials processing. The cold spray coatings had an average value of 57 Brinell, while that of fully hardened wrought Al was 45 Brinell. The more extensive plastic deformation of each particle as it impacts the surface of the substrate during the cold spray process results in microstructural changes that increase the hardness. It has been well established that cold spray is considered to be a powder shock compaction and consolidation process resulting in high localized strain and substantial grain refinement via fracturing or the formation of sub-grain structures (11–13). Therefore, an increase

in hardness, commensurate with the amount of plastic deformation of each particle during consolidation, was anticipated. Even though this consolidation theory has been associated with the deposition of powder mixtures, it is apparent that as a result of the high localized strain that occurs within each particle during impact such conditions were satisfied for significant grain refinement.

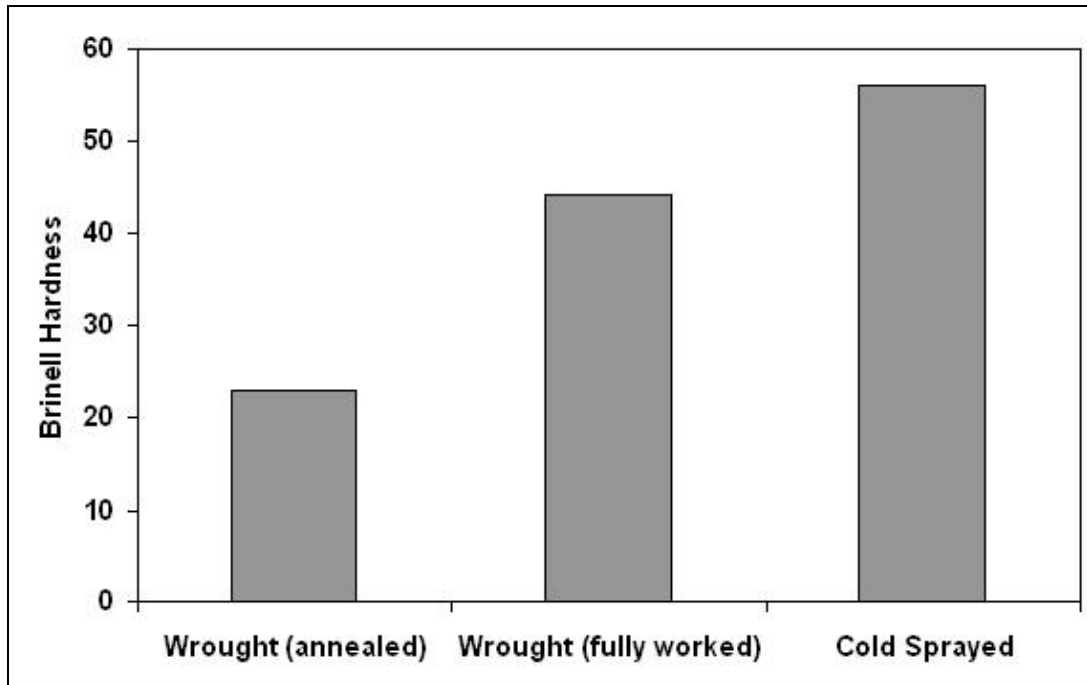


Figure 7. Hardness of Al cold spray coatings.

5.4 Microstructural Examination

The microstructural features of the CP-Al cold spray coatings were examined utilizing optical and electron microscopy. Cold spray coatings were produced with the high pressure Ktech system and the high pressure ARL system using both helium and nitrogen for comparative purposes. Figure 8 shows a representative micrograph of the filling of an indentation with CP-Al using helium gas at room temperature and at a gas pressure of 2.74 MPa with the ARL portable system. The coating is very dense and shows no evidence of significant inherent material defects. The coating/substrate interface is free from voids, entrapped grit, or areas of delamination. The coating material is in intimate contact with the substrate forming a metallurgical bond as a result of the severe plastic deformation during accelerated particle impact (14).

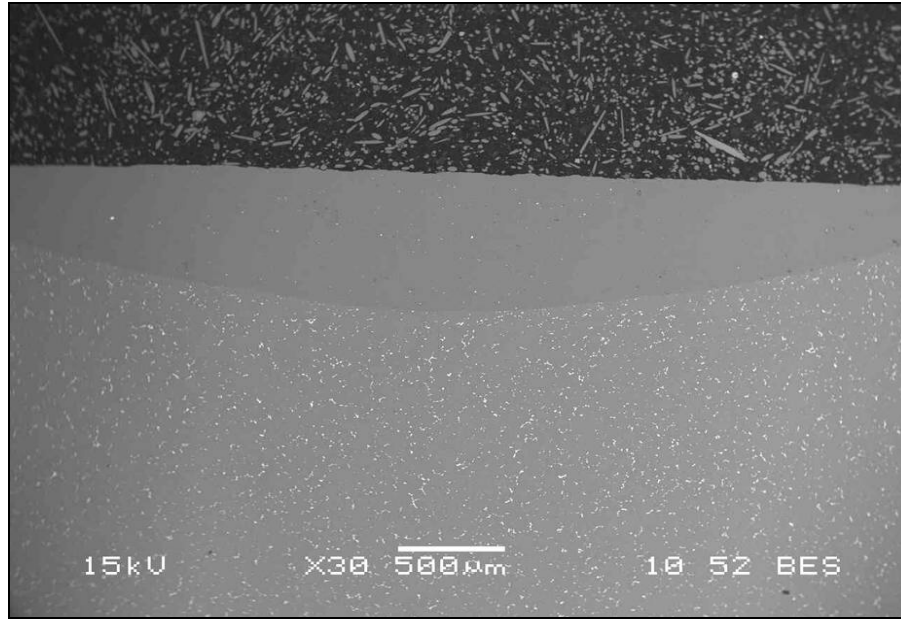


Figure 8. Al deposited on Mg by the ARL portable cold spray system.

Figure 9 shows a higher magnification of figure 8, but subsequent to etching with Keller's reagent. There was evidence of plastic deformation of the consolidated particles and significant grain refinement that was the result of the shock compression occurring during particle impact causing grain size reduction (15).

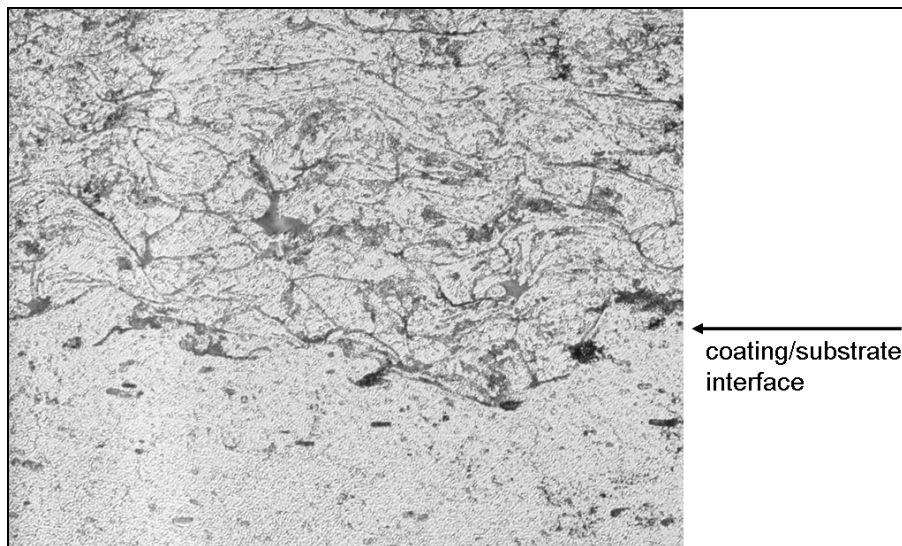


Figure 9. Etched sample showing grain refinement and plastic deformation.

Figure 10 is an example of a coating produced with the Ktech high pressure stationary system also using helium gas at a temperature of 400 °C and a pressure of 2.74 MPa. The figure clearly illustrates the potential of cold spray to produce an adherent and dense Al 5056 coating. The microstructure is free from voids and porosity and the interface between the coating and the substrate is barely discernable.

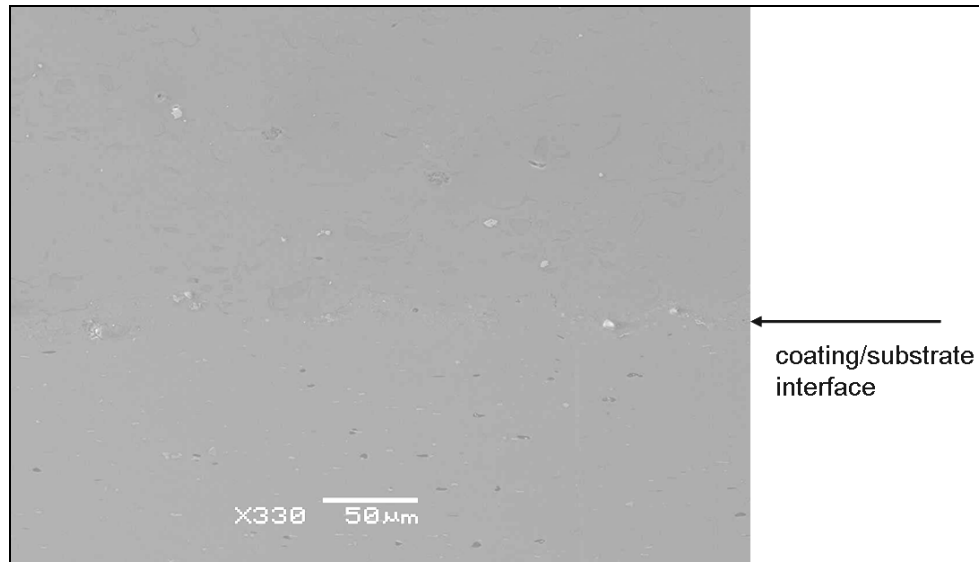


Figure 10. 5056 Al alloy deposited using helium as the carrier gas.

Figure 11 shows a representative example of a cold spray CP-Al coating deposited using nitrogen as the carrier gas at a temperature of 250 °C and a gas pressure of 2.74 MPa. The resultant coating was porous and had low bond strength, because the gas temperature could not be increased until the incorporation of a plastic nozzle that prevented nozzle fouling. Figures 12 and 13 show significant improvement of the coating when the gas temperature was increased to 400 °C. The density had improved as a result of the higher particle velocity as had the quality of the interface between the coating and the substrate.

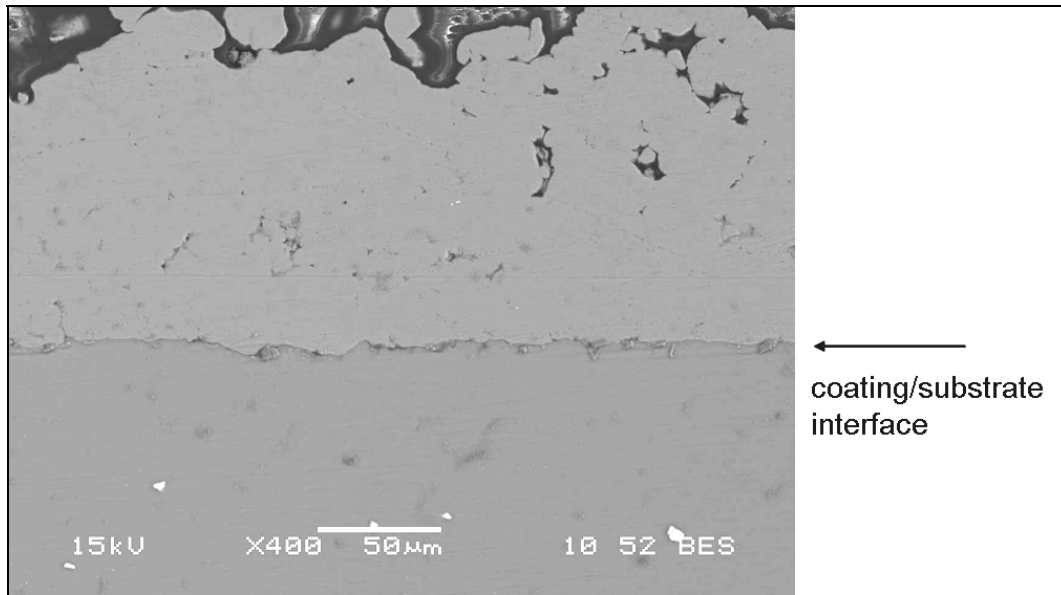


Figure 11. Al deposited using nitrogen as the carrier gas at 250 °C.

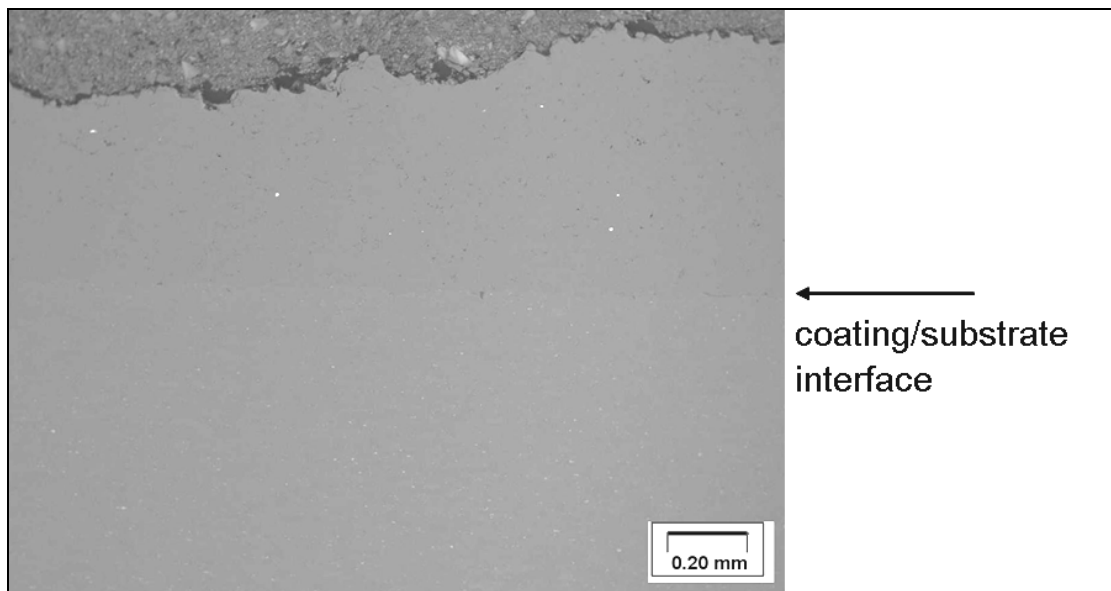


Figure 12. Al deposited using nitrogen as the carrier gas at 400 °C.

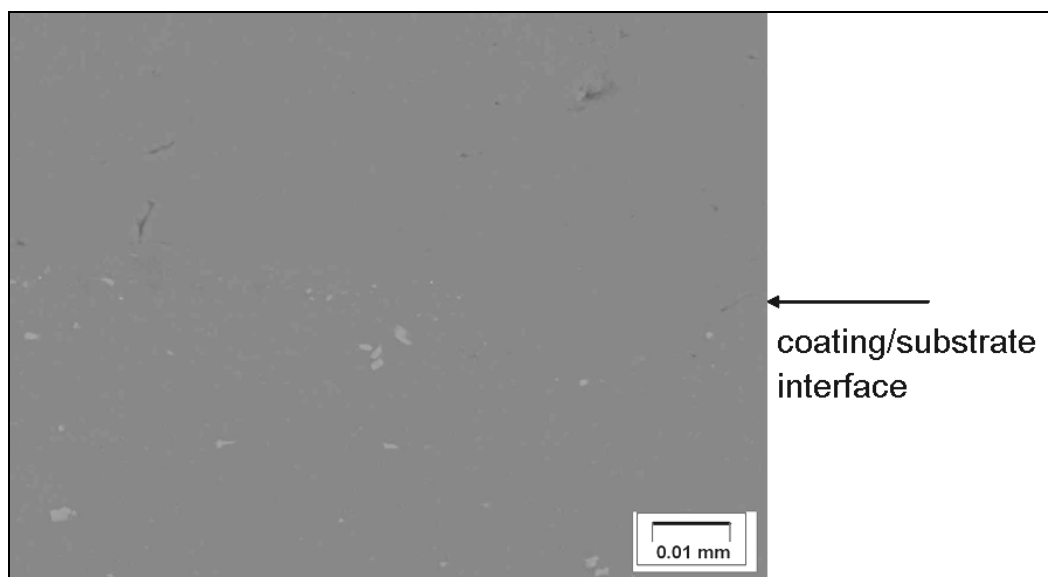


Figure 13. Higher magnification Al deposited using nitrogen at 400 °C.

5.5 Corrosion Testing

The requirement for salt fog exposure established by the Corpus Christi Army Depot (CCAD) and the Naval Air Depot (NADEP), Cherry Point, is a minimum of 336 h according to the requirements of ASTM B117, “Standard Practice for Operating Salt Spray (Fog) Apparatus.” A total of three test panels of ZE-41A Mg (7.62 cm by 10.16 cm by 0.64 cm) were machined from a plate, degreased, and then grit blasted lightly with 60 grit Al_2O_3 that was free of any contamination. This is important as any iron contamination can adversely affect corrosion test results. The panels were subsequently coated with 0.30–0.375 mm (0.012–.015 in.) of CP-Al via cold spray. The carrier gas was helium, the pressure was 2.74 MPa, the traverse rate was 100 mm/s, the feed rate was 2 g/min, and the standoff distance was 25 mm.

The test panels were placed into a salt fog chamber operating at 35 °C with a 5% salt solution and periodically examined every 4 h. The lacquer applied to the edges of the test panels of Mg failed prematurely, allowing corrosion to take place from a few areas on the edges of the panels. When this occurred, the specific Mg test panels were removed from the salt fog chamber and the edges were cleaned, recoated with lacquer, and corrosion testing was resumed. These Mg panels had to be repaired in this manner several times during corrosion testing, but after 504 h, the repair procedure could not be attempted again since too much of the Mg substrate had corroded away from the edges and back side of the test panels. However, the minimum acceptance requirement of 336 h had been achieved. Figure 14 shows the Al cold sprayed coupons after 336 h in the salt spray chamber.

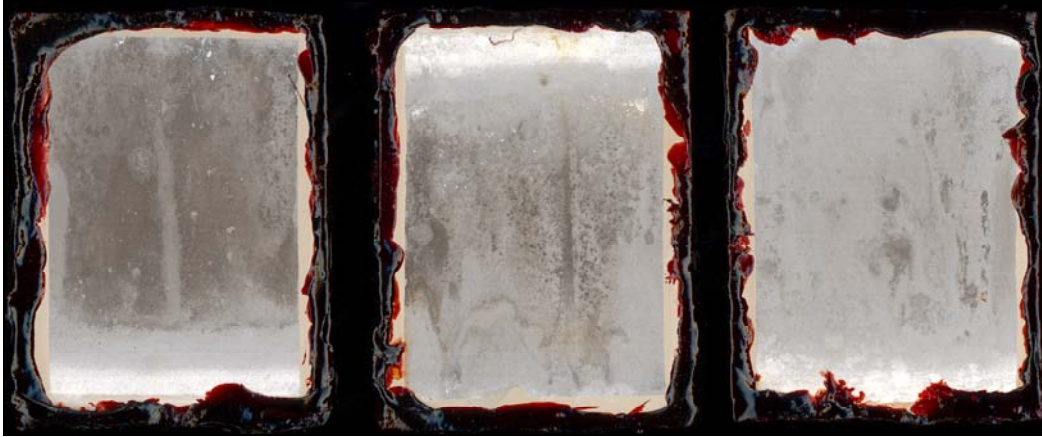


Figure 14. Al-coated Mg panels after exposure in salt fog chamber.

Another set of five CP-Al Mg panels were deposited using nitrogen gas at 250 °C and a pressure of 2.74 MPa. This was the highest nitrogen gas temperature that could be employed using a metal nozzle without nozzle clogging. These panels were subjected to the same salt fog spray conditions but due to the porous nature of the coating as shown in figure 11, the Al coating failed after only 8 h. The failed panels are shown in figure 15. A close-up of a resultant corrosion product protrusion from a pinhole in the Al coating is shown in figure 16.



Figure 15. Panels sprayed using 350 °C nitrogen gas after 8 h of exposure.



Figure 16. Corrosion product growth resulting from a pinhole in the Al coating.

A third set of corrosion test panels were prepared but the test panels were machined to round off sharp edges and corners. All of the exposed coupon surfaces (front, back, and edges) were coated with cold sprayed CP-Al. In addition, a proprietary thermoplastic nozzle was used for these deposits, allowing a higher nitrogen gas temperature to be used. A nitrogen carrier gas temperature of 400 °C and a pressure of 2.74 MPa were used. A line-to-line index of 1 mm was used for one of the panels and a 0.5 mm index was used for the other panel. The edges of the panels were sealed with epoxy so only the front and back surfaces were exposed to the salt spray. The panels with epoxy sealed edges, shown in figure 18, were exposed for 804 h (0.5 mm coupon) and 1,000 h (1 mm coupon). Except for some discoloration of the Al, no corrosion is evident on the Al or the Mg. However, upon inspection, a pinhole in the epoxy coating was found in each of the epoxy coated coupons. The pinholes in the epoxy coating have been repaired and the panels have been returned to the salt spray chamber for further exposure. Figures 17 and 18 show these panels before and after salt spray exposure.

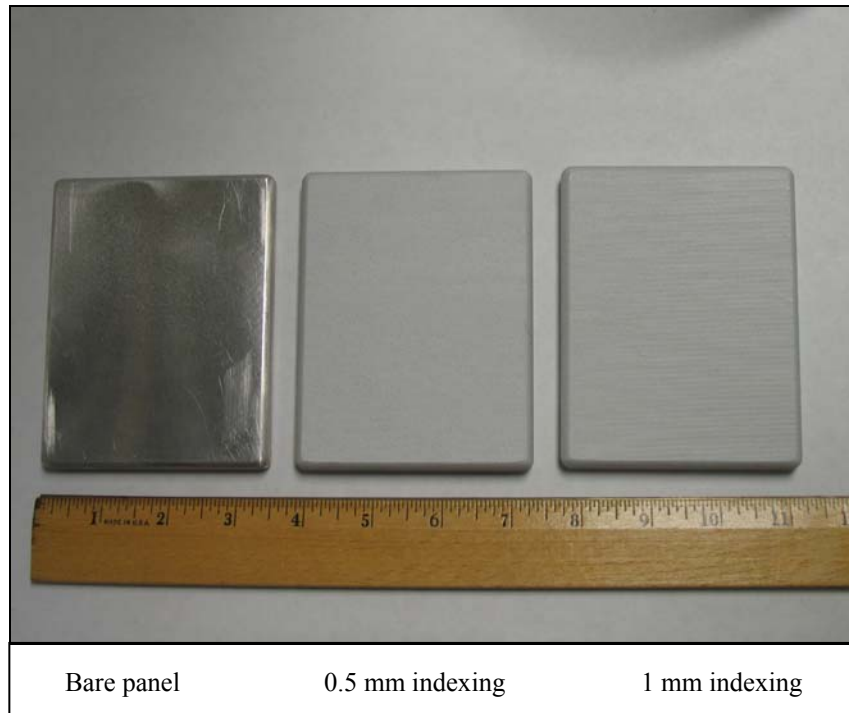


Figure 17. Mg panels before exposure.

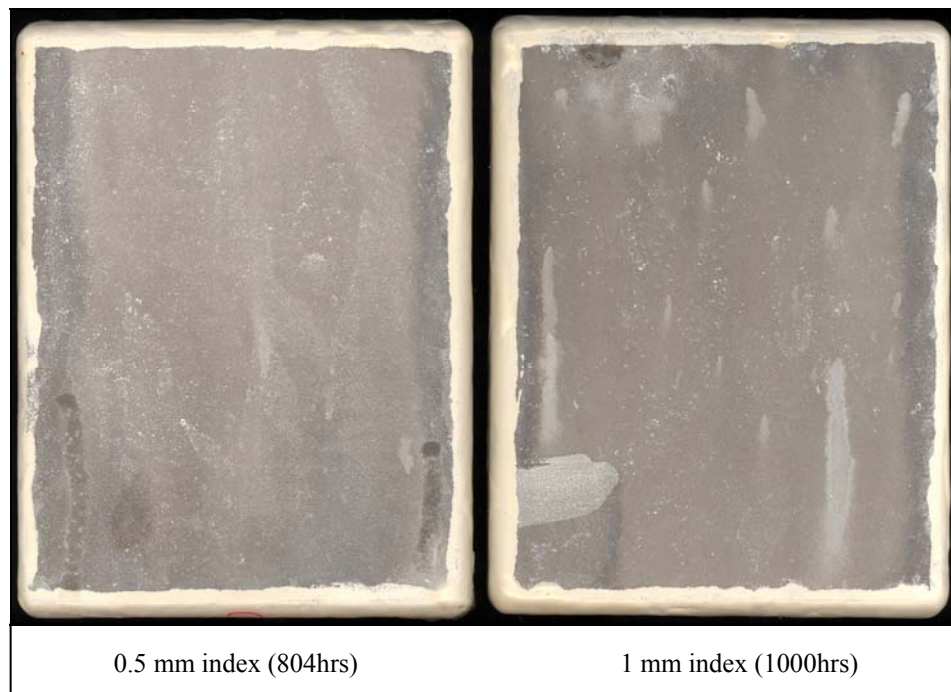


Figure 18. Al-coated Mg panels with epoxy coated edges after salt spray exposure.

5.6 Oxide Analysis

Inert gas fusion, according to ASTM E1019, was used to analyze the oxygen content of a CP-Al deposit produced by cold spray. These results were subsequently compared to the oxygen content of the starting powder. In this test, the starting powder consisted of CP-Al, -325 mesh (figure 19). The results revealed that the cold spray deposit did contain less oxygen (0.25%) as compared to the powder (0.34%). The reason for this decrease is that the brittle oxide layer on each particulate fractures during deposition as a result of the extreme amount of plastic deformation, and a portion of it falls away, never being incorporated into the deposit. The oxygen content of the CP-Al cold spray coating is largely determined by the oxygen content of the original powder, not the process.

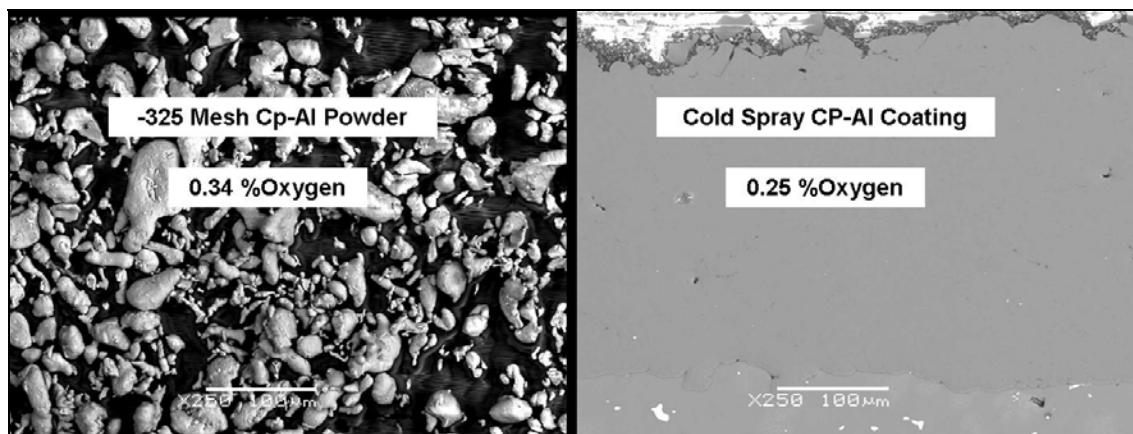


Figure 19. Oxygen content measured by inert gas fusion.

6. Discussion

In recent years, experimental and computational studies at universities such as Helmut Schmidt University in Hamburg, Germany, have led to a better understanding of the cold spray process (16). Modeling of the particle impact and bonding mechanisms has been performed as well as measurements of the effect of process variables on particle temperatures and velocities. For the former, a number of researchers have likened the bonding mechanisms in cold spray with those identified in explosive welding, where bond formation relies on deformation under high pressures (17). With respect to process variables, helium or nitrogen are the most commonly used gases for cold spray, with higher particle velocities obtained with helium, but nitrogen is generally preferred because it is much less expensive. The results of this study have shown this to be the case in that adequate adhesion, density, and corrosion resistance can be achieved with the use of nitrogen for the deposition of CP-Al.

The feasibility of using the cold spray process to repair nonstructural Mg aircraft components has been demonstrated by the satisfactory results obtained from adhesion, corrosion testing, and microstructural analysis. The cold spray process yielded adhesion values in excess of 58.6 MPa when helium was used as the carrier gas and 59.8 MPa when nitrogen was employed. These values represent the strength of the adhesive used, as all failures occurred at the interface between the glue and the coating. The cold spray coating was not pulled off of the substrate and the coating did not fail cohesively.

The cold spray coating was required to withstand a minimum of 336 h of salt fog exposure according to the requirements of ASTM B117. The CP-Al coating applied by cold spray on ZE-41A Mg test panels to a thickness of 0.305–0.381 mm using helium as the carrier gas lasted at least 610 h before the lacquer used to seal the edges and back face of the test panel failed. The coating was still intact and did not fail from the front face of the test panel. These results serve as a testimony that adherent and dense coatings can be achieved by the cold spray process for this application. An additional set of ZE-41A Mg panels coated with CP-Al using nitrogen gas are currently being tested in the B117 Salt Fog Spray Chamber and have exceeded 1,000 h (figure 15).

7. Conclusions

The cold spray process has matured from an emerging technology to a viable alternative to thermal spray for selected applications (18). This study has shown it to be a promising, cost-effective, and environmentally acceptable technology to impart surface protection and restore dimensional tolerances to Mg alloy components on helicopters and fixed-wing aircraft.

References

1. Levy, M.; Bombard, R.; Huie, R. Assessment of Some Corrosion Protection Schemes For Magnesium Alloy ZE41A-T5. *Proceedings of the Tri-Service Corrosion Conference*, pp 154–167.
2. Yamauchi, M.; Seki, J.; Sakita, E.; Miyata, Y.; Arita, K. Corrosion Resistant Composite Layer on Magnesium Alloys. *Advanced Composite Materials* **1991**, 1 (1), 3–10.
3. Gonzalez-Nunez, M.; Nunez-Lopez, C.; Skeldon, P.; Thompson, G.; Karimzadeh, H.; Lyon, P.; Wilks, T. A Non-Chromate Conversion Coating for Magnesium Alloys and Magnesium-Based Metal Matrix Composites. *Corrosion Science* **1995**, 37 (11), 1763–1772.
4. Gorman, W.; Woolsey, E. Selective Anodization Process for Repair of Magnesium Helicopter Components. *Proceedings of the Tri Service Corrosion Conference*, 2003.
5. Griffin, R.; Zuniga, D. Evaluation of Coatings on Mg Alloy ZE41A Used in Helicopter Rotor Gearboxes, *Proceedings of the Tri Service Corrosion Conference*, 2005.
7. Johnson, A. Helium Recycle – A Viable Industrial Option for Cold Spray. *Proceedings of the Cold Spray Conference*, Akron, OH, ASM International, 2004.
8. Vlcek, J.; Gimeno L.; Huber, H.; Lugscheider, E. A Systematic Approach to Material Eligibility for the Cold Spray Process. *J. of Thermal Spray Technology* **2005**, 14 (1), 125–133.
9. Champagne, V.; Helfrich, D.; Leyman, P.; Grendahl, S.; Klotz, B. Interface Material Mixing Formed by the Deposition of Copper on Aluminum by Means of the Cold Spray Process. *J. of Thermal Spray Technology*, 14 (3), 330–334.
10. Properties and Selection: Nonferrous Alloys and Special-Purpose Materials. In *ASM Handbook*, 10th ed., vol. 2; ASM International: Materials Park, OH, 1990, p 49.
11. Stoltenhoff, T.; Kreye, H.; Krommer, W.; Richter, H. *Cold Spraying-from Thermal Spraying to High Kinetic Energy Spraying*, HVOF Colloquium 2000, Gemeinschaft Thermisches Spritzen e.V., 2000, 29–38.
12. Stoltenhoff, T.; Kreye, H.; Richter, H.; Assadi, H. Optimization of the Cold Spray Process. ITSC 2001, C.C. Berndt and E.F. Lugscheider, *ASM International* **2001**, 409–416.
13. McCune, R.; Donlon, W.; Popoola, O.; Cartwright, E. Characterization of Copper Layers Produced by Cold Gas-Dynamic Spraying. *J. of Thermal Spray Technology* **2000**, 9 (1), 73–82.

14. Maev, R; Leshchynsky, V; Papyrin, A. Structure Formation of Ni-based Composite Coatings During Low Pressure Gas Dynamic Spraying. *Proceedings of the 2006 International Thermal Spray Conference*, ASM International, Seattle, WA, 2006.
15. Sawaoka, A.B. Graham, R and Thadhani, N. In *Shock Waves in Materials Science*, Springer-Verlag: Berlin, 1993, pp 35–65.
16. Kreye, H. The Cold Spray Process and Its Potential for Industrial Applications. *Proceedings of Cold Spray 2004*, The Thermal Spray Society of ASM International, Akron, OH, 2004.
17. Zhang, D.; Shipway, P.; McCartney, D. Cold Gas Dynamic spraying of Aluminum: The Role of Substrate Characteristics in Deposit Formation. *J. of Thermal Spray Technology* **2005**, *14* (1), 109–116.
18. Papyrin, A. Cold Spray Technology. *Advanced Materials and Processes* **2001**, *159* (9), 49–51.

Acronyms

Al 5056	Al alloy 5056
Al	aluminum
Al-12Si	Al-12% silicon alloy
Al ₂ O ₃	aluminum oxide
ARL	U.S. Army Research Laboratory
ARL-CCST	ARL Center for Cold Spray Technology
ASTM	American Society for Testing and Materials
CCAD	Corpus Christi Army Depot
CP-Al	commercially pure aluminum
Cr	chromium
DoD	Department of Defense
DSTO	Defense Systems and Technology Operation
GMD	geometric mean diameter
Mg	magnesium
Mn	manganese
NADEP	Naval Air Depot
NCMS	National Center for Manufacturing Sciences
R&D	research and development
WC	tungsten carbide

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